

## PATENT ABSTRACTS OF JAPAN

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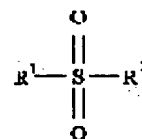
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(54) NON-AQUEOUS ELECTROLYTE AND LITHIUM SECONDARY BATTERY USING IT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium secondary battery equipped with excellent cycle characteristic, electric capacity, charged condition holding characteristic.

SOLUTION: A lithium secondary battery includes a non-aqueous electrolytic solution formed by dissolving electrolyte in a non-aqueous solvent and containing a sulfonic derivative expressed by a general formula, where R<sup>1</sup> and R<sup>2</sup> are respectively and independently phenyl radical, benzyl radical, tolyl radical, alkyl radical of a carbon number 1-12 and cycloalkyl radical of a carbon number 3-6.



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the nonaqueous electrolyte which can offer the lithium secondary battery excellent also in cell properties, such as the cycle property of a cell, and electric capacity, a preservation property, and the lithium secondary battery using it.

[0002]

[Description of the Prior Art] In recent years, the lithium secondary battery is widely used as power supplies for a drive, such as small electronic equipment. Mainly, negative-electrode - composition of is done and, as for the lithium secondary battery, a positive electrode, nonaqueous electrolyte, and the lithium secondary battery that made lithium multiple oxides, such as  $\text{LiCoO}_2$ , the positive electrode, and used the carbon material or the lithium metal as the negative electrode are used especially suitably. And as nonaqueous electrolyte for the lithium secondary batteries, carbonate, such as ethylene carbonate (EC) and propylene carbonate (PC), is used suitably.

[0003]

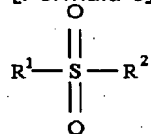
[Problem(s) to be Solved by the Invention] However, the rechargeable battery which has the further excellent property about cell properties, such as the cycle property of a cell and electric capacity, is called for. When the solvent in nonaqueous electrolyte carries out oxidative degradation of the part locally at the time of charge, the lithium secondary battery using  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , etc. as a positive electrode produces cell performance degradation, in order that this decomposition product may check the desirable electrochemical reaction of a cell. This is considered to originate in the electrochemical oxidation of the solvent in the interface of positive-electrode material and nonaqueous electrolyte. Moreover, while lithium secondary batteries using the high-crystallized carbon material, such as a natural graphite and an artificial graphite, repeat charge and discharge also in EC for which the solvent in nonaqueous electrolyte carries out reduction decomposition on a negative-electrode front face at the time of charge, and is generally widely used as a nonaqueous electrolyte solvent at it as a negative electrode, reduction decomposition takes place in part, and cell performance degradation happens. For this reason, the present condition is that cell properties, such as the cycle property of a cell and electric capacity, are not necessarily satisfactory.

[0004] this invention aims at offering the nonaqueous electrolyte for lithium secondary batteries which can constitute the lithium secondary battery which solved the technical problem about the above nonaqueous electrolyte for lithium secondary batteries, was excellent in the cycle property of a cell, and was further excellent also in cell properties, such as electric capacity and a preservation property in a charge state, and the lithium secondary battery using it.

[0005]

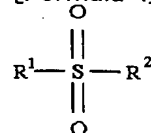
[Means for Solving the Problem] It sets to the nonaqueous electrolyte by which the electrolyte is dissolved in the non-aqueous solvent, and this invention is the following general formula (I) in this nonaqueous electrolyte.

[Formula 3]



(—  $\text{R}^1$  and  $\text{R}^2$  show independently a phenyl group, a benzyl, a tolyl group, the alkyl group of carbon numbers 1–12, and the cycloalkyl machine of carbon numbers 3–6 among a formula, respectively It is related with the nonaqueous electrolyte characterized by the sulfone derivative expressed with) containing. Moreover, it sets to the lithium secondary battery which consists of nonaqueous electrolyte by which the electrolyte is dissolved in the positive electrode, the negative electrode, and the non-aqueous solvent, and this invention is the following general formula (I) in this nonaqueous electrolyte.

[Formula 4]



(— R1 and R2 show independently a phenyl group, a benzyl, a tolyl group, the alkyl group of carbon numbers 1–12, and the cycloalkyl machine of carbon numbers 3–6 among a formula, respectively It is related with the lithium secondary battery characterized by the sulfone derivative expressed with) containing.

[0006] The nonaqueous electrolyte of this invention is used as a composition member of a lithium secondary battery. Especially about composition members other than the nonaqueous electrolyte which constitutes a rechargeable battery, it is not limited but the various composition members currently used conventionally can be used.

[0007]

[Embodiments of the Invention] In the sulfone derivative expressed with the aforementioned general formula (I) contained in the nonaqueous electrolyte by which the electrolyte is dissolved in the non-aqueous solvent, R1 and R2 become independent, respectively, and a phenyl group, a benzyl, and its an aromatic substituent like a tolyl group are desirable. Furthermore, an aliphatic substituent like the alkyl group of carbon numbers 1–12 and the cycloalkyl machine of carbon numbers 3–6 is sufficient.

[0008] As an example of a sulfone derivative expressed with the aforementioned general formula (I), diphenylsulfone, a dibenzyl sulfone, a G p-tolyl sulfone, a di-n-butyl sulfone, a G iso-butyl sulfone, a G tert-butyl sulfone, a dicyclohexyl sulfone, etc. are mentioned, for example.

[0009] Since sufficient cell performance which the cell performance might fall and was expected to be too few will not be obtained if many [ too ], the content of a sulfone derivative expressed with the aforementioned general formula (I) contained in nonaqueous electrolyte has 0.01 – 0.6% of the weight of an especially desirable range 0.001 to 2% of the weight to the weight of nonaqueous electrolyte.

[0010] As a non-aqueous solvent used by this invention, what consists of a high dielectric constant solvent and a hypoviscosity solvent is desirable. As a high dielectric constant solvent, annular carbonate, such as ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC), is mentioned suitably, for example. These high dielectric constant solvents may be used by one kind, and you may use them, combining them two or more kinds.

[0011] As a hypoviscosity solvent, amides, such as ester, such as nitril, such as lactone, such as ether, such as chain-like carbonate [ such as dimethyl carbonate (DMC), methylethyl carbonate (MEC), and diethyl carbonate (DEC), ], tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 4-dioxane, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, 1, and 2-dibutoxy ethane, and gamma-butyrolactone, and an acetonitrile, and a methyl propionate, and a dimethylformamide, are mentioned, for example. These hypoviscosity solvents may be used by one kind, and you may use them, combining them two or more kinds. A high dielectric constant solvent and a hypoviscosity solvent are chosen as arbitration, respectively, and are combined and used. in addition, an aforementioned high dielectric constant solvent and an aforementioned hypoviscosity solvent — a capacity factor (high dielectric constant solvent : hypoviscosity solvent) — usually — 1.9–4:1 — 1:4–7:3 come out comparatively preferably, and it is used

[0012] As an electrolyte used by this invention,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ ,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ , etc. are mentioned, for example. These electrolytes may be used by one kind, and you may use them, combining them two or more kinds. 0.1–3 M of these electrolytes is usually preferably used by the concentration of 0.5–1.5M, dissolving in the aforementioned non-aqueous solvent.

[0013] The nonaqueous electrolyte of this invention is obtained by mixing an aforementioned high dielectric constant solvent and an aforementioned hypoviscosity solvent, dissolving the aforementioned electrolyte in this, and dissolving the sulfone derivative expressed with the aforementioned general formula (I).

[0014] For example, the compound metallic oxide of the at least one kind of metal and the lithium which are chosen from the group which consists of cobalt, manganese, nickel, chromium, iron, and vanadium as a positive active material is used. As such a compound metallic oxide,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , etc. are mentioned, for example.

[0015] the positive active material of the above [ a positive electrode ] — binders, such as electric conduction agents, such as acetylene black and carbon black, a polytetrafluoroethylene (PTFE), and a polyvinylidene fluoride (PVDF), and a solvent — kneading — a positive electrode — after considering as a mixture, this positive-electrode material is applied to the lath board of the aluminum foil as a charge collector, or the product made from stainless steel, and it is produced after dryness and pressurization molding by heat-treating under a vacuum at the temperature of 50 degrees C – about 250 degrees C for about 2 hours

[0016] Matter, such as a carbon material [the pyrolytic carbons, the corks, the graphite, the organic high-molecular-compounds (artificial-graphite, natural graphite, etc.) combustion object, and the carbon fiber], a compound stannic-acid ghost, etc. which have the graphite-mold crystal structure which can emit occlusion and ] a lithium metal, a lithium alloy, and a lithium as a negative-electrode active material, is used. It is desirable to use the carbon material which has especially the graphite-mold crystal structure whose spacing (d002) of a lattice plane (002) is 0.335–0.340nm (nano meter). in addition, powder material like a carbon material — binders, such as an ethylene-propylene-diene terpolymer (EPDM), a polytetrafluoroethylene (PTFE), and a polyvinylidene fluoride (PVDF), — kneading — a negative electrode — it is used as a mixture

[0017] Especially the structure of a lithium secondary battery is not limited and the coin type cell which has the separator of a positive electrode, a negative electrode and a monolayer, or a double layer, a cylindrical cell, a square shape cell which has the separator of the shape of a positive electrode, a negative electrode, and a roll further, etc. are mentioned as an example. In addition, the fine porous membrane of a polyolefine well-known as separator, textile fabrics, a nonwoven fabric, etc. are used.

[0018]

[Example] Next, an example and the example of comparison are given and this invention is explained concretely.

After having prepared the non-aqueous solvent of example 1 [manufacture of nonaqueous electrolyte] EC:DMC(capacity factor) =1:2, having dissolved so that it might become the concentration of 1M about LiPF<sub>6</sub> at this, and preparing nonaqueous electrolyte, diphenylsulfone [an R<sub>1</sub>=R<sub>2</sub>= phenyl group] was further added as a sulfone derivative (additive) so that it might become 0.1 % of the weight to nonaqueous electrolyte.

[0019] [Production of a lithium secondary battery and measurement of a cell property] What mixed acetylene black (electric conduction agent) 10% of the weight 80% of the weight, mixed the polyvinylidene fluoride (binder) at 10% of the weight of a rate, added the 1-methyl-2-pyrrolidone solvent to this, and was mixed was applied on the aluminum foil, it dried, LiCoO<sub>2</sub> (positive active material) was pressurization-cast, it heat-treated, and the positive electrode was prepared. It dried and pressurization-cast, applied what mixed the natural graphite (negative-electrode active material) 90% of the weight, mixed the polyvinylidene fluoride (binder) at 10% of the weight of a rate, added the 1-methyl-2-pyrrolidone solvent to this, and was mixed on copper foil and heat-treated, and the negative electrode was prepared. And using the separator of a polypropylene fine porosity film, the above-mentioned nonaqueous electrolyte was made to pour in and the coin cell (3.2mm in the diameter of 20mm, thickness) was produced. Using this coin cell, under the room temperature (20 degrees C), it charged to final-voltage 4.2V for 5 hours, and, next, discharged to final-voltage 2.7V under the 0.8mA constant current, and this charge and discharge were repeated by the 0.8mA constant current and the constant voltage. Initial charge-and-discharge capacity is 1M. It was almost equivalent to the case (example 1 of comparison) where LiPF<sub>6</sub>+EC-DMC (1/2) is used as nonaqueous electrolyte (with no additive), and when the cell property after 50 cycles was measured, the service-capacity maintenance factor when making initial service capacity into 100% was 92.2%. Moreover, the low-temperature property was also good. The production conditions and cell property of a coin cell are shown in Table 1.

[0020] When used diphenylsulfone [an R<sub>1</sub>=R<sub>2</sub>= phenyl group] 0.4% of the weight to nonaqueous electrolyte as example 2 additive, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 89.7%. The production conditions and cell property of a coin cell are shown in Table 1.

[0021] When used diphenylsulfone [an R<sub>1</sub>=R<sub>2</sub>= phenyl group] 0.02% of the weight to nonaqueous electrolyte as example 3 additive, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 90.8%. The production conditions and cell property of a coin cell are shown in Table 1.

[0022] When used the G p-tolyl sulfone [an R<sub>1</sub>=R<sub>2</sub>=p-tolyl group] 0.1% of the weight to nonaqueous electrolyte as example 4 additive, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 91.9%. The production conditions and cell property of a coin cell are shown in Table 1.

[0023] When used the di-n-butyl sulfone [an R<sub>1</sub>=R<sub>2</sub>=n-butyl] 0.1% of the weight to nonaqueous electrolyte as example 5 additive, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 91.6%. The production conditions and cell property of a coin cell are shown in Table 1.

[0024] The non-aqueous solvent of example 6 EC:PC:DMC(capacity factor) =1:1:2 was prepared, and after having dissolved so that it might become the concentration of 1M about LiPF<sub>6</sub> at this, and adjusting nonaqueous electrolyte, diphenylsulfone [an R<sub>1</sub>=R<sub>2</sub>= phenyl group] was further added so that it might become 0.1 % of the weight to nonaqueous electrolyte. When the coin cell was produced like the example 1 using this nonaqueous electrolyte and the cell property was measured, initial service capacity was almost equivalent to the case (example 1 of comparison) where only EC-DMC (capacity factors 1/2) is used as nonaqueous electrolyte, and when the cell property after 50 cycles was measured, the service-capacity maintenance factor when making initial service capacity into 100% was 92.3%. Moreover, the low-temperature property was also good. The production conditions and cell property of a coin cell are shown in Table 1.

[0025] When replaced with the natural graphite, and used the artificial graphite as an example 7 negative-electrode active material, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 88.2%. The production conditions and cell property of a coin cell are shown in Table 1.

[0026] When replaced with LiCoO<sub>2</sub>, and used LiMn 2O<sub>4</sub> as example 8 positive active material, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 91.4%. The production conditions and cell property of a coin cell are shown in Table 1.

[0027] The non-aqueous solvent of example of comparison 1 EC:DMC(capacity factor) =1:2 was prepared, and it dissolved so that it might become the concentration of 1M about LiPF<sub>6</sub> at this. At this time, the sulfone derivative was not added at all. The coin cell was produced like the example 1 using this nonaqueous electrolyte, and the cell property was measured. The service-capacity maintenance factor after 50 cycles was 83.8% to initial service capacity. The production conditions and cell property of a coin cell are shown in Table 1.

[0028]

[Table 1]

	正極	負極	添加剤	添加量 wt%	電解液組成 (容量比)	50 サイクル 放電容量維持率 %
実施 例 1	LiCoO <sub>2</sub>	天然 黒鉛	ジフェニル スルホン	0.1	1M LiPF <sub>6</sub> EC/DMC=1/2	92.2
実施 例 2	LiCoO <sub>2</sub>	天然 黒鉛	ジフェニル スルホン	0.4	1M LiPF <sub>6</sub> EC/DMC=1/2	89.7
実施 例 3	LiCoO <sub>2</sub>	天然 黒鉛	ジフェニル スルホン	0.02	1M LiPF <sub>6</sub> EC/DMC=1/2	90.8
実施 例 4	LiCoO <sub>2</sub>	天然 黒鉛	ジ-p-トリル スルホン	0.1	1M LiPF <sub>6</sub> EC/DMC=1/2	91.9
実施 例 5	LiCoO <sub>2</sub>	天然 黒鉛	ジ-n-ブチル スルホン	0.1	1M LiPF <sub>6</sub> EC/DMC=1/2	91.6
実施 例 6	LiCoO <sub>2</sub>	天然 黒鉛	ジフェニル スルホン	0.1	1M LiPF <sub>6</sub> EC/PC/DMC=1/1/2	92.3
実施 例 7	LiCoO <sub>2</sub>	人 造 黒鉛	ジフェニル スルホン	0.1	1M LiPF <sub>6</sub> EC/DMC=1/2	88.2
実施 例 8	LiMn <sub>2</sub> O <sub>4</sub>	天然 黒鉛	ジフェニル スルホン	0.1	1M LiPF <sub>6</sub> EC/DMC=1/2	91.4
比較 例 1	LiCoO <sub>2</sub>	天然 黒鉛	なし	0	1M LiPF <sub>6</sub> EC/DMC=1/2	83.8

[0029] In addition, this invention is not limited to the example of a publication, but various combination which can be guessed is easily possible for it from the meaning of invention. Especially the combination of the solvent of the above-mentioned example is not limited. Furthermore, although the above-mentioned example is related with a coin cell, this invention is applied also to the cell of cylindrical shape and prism type.

[0030]

[Effect of the Invention] According to this invention, the lithium secondary battery excellent in cell properties, such as the cycle property of a cell, electric capacity, and a preservation property, can be offered.

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**TECHNICAL FIELD**

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[The technical field to which invention belongs] this invention relates to the nonaqueous electrolyte which can offer the lithium secondary battery excellent also in cell properties, such as the cycle property of a cell, and electric capacity, a preservation property, and the lithium secondary battery using it.

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**PRIOR ART**

[Description of the Prior Art] In recent years, the lithium secondary battery is widely used as power supplies for a drive, such as small electronic equipment. Mainly, negative-electrode - composition of is done and, as for the lithium secondary battery, a positive electrode, nonaqueous electrolyte, and the lithium secondary battery that made lithium multiple oxides, such as  $\text{LiCoO}_2$ , the positive electrode, and used the carbon material or the lithium metal as the negative electrode are used especially suitably. And as nonaqueous electrolyte for the lithium secondary batteries, carbonate, such as ethylene carbonate (EC) and propylene carbonate (PC), is used suitably.

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**EFFECT OF THE INVENTION**

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] However, the rechargeable battery which has the further excellent property about cell properties, such as the cycle property of a cell and electric capacity, is called for. When the solvent in nonaqueous electrolyte carries out oxidative degradation of the part locally at the time of charge, the lithium secondary battery using  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , etc. as a positive electrode produces cell performance degradation, in order that this decomposition product may check the desirable electrochemical reaction of a cell. This is considered to originate in the electrochemical oxidation of the solvent in the interface of positive-electrode material and nonaqueous electrolyte. Moreover, while lithium secondary batteries using the high-crystallized carbon material, such as a natural graphite and an artificial graphite, repeat charge and discharge also in EC for which the solvent in nonaqueous electrolyte carries out reduction decomposition on a negative-electrode front face at the time of charge, and is generally widely used as a nonaqueous electrolyte solvent at it as a negative electrode, reduction decomposition takes place in part, and cell performance degradation happens. For this reason, the present condition is that cell properties, such as the cycle property of a cell and electric capacity, are not necessarily satisfactory. [0004] this invention aims at offering the nonaqueous electrolyte for lithium secondary batteries which can constitute the lithium secondary battery which solved the technical problem about the above nonaqueous electrolyte for lithium secondary batteries, was excellent in the cycle property of a cell, and was further excellent also in cell properties, such as electric capacity and a preservation property in a charge state, and the lithium secondary battery using it.

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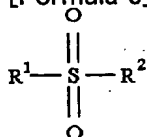
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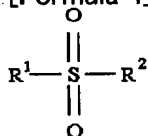
[Means for Solving the Problem] It sets to the nonaqueous electrolyte by which the electrolyte is dissolved in the non-aqueous solvent, and this invention is the following general formula (I) in this nonaqueous electrolyte.

[Formula 3]



(— R1 and R2 show independently a phenyl group, a benzyl, a tolyl group, the alkyl group of carbon numbers 1-12, and the cycloalkyl machine of carbon numbers 3-6 among a formula, respectively It is related with the nonaqueous electrolyte characterized by the sulfone derivative expressed with) containing. Moreover, it sets to the lithium secondary battery which consists of nonaqueous electrolyte by which the electrolyte is dissolved in the positive electrode, the negative electrode, and the non-aqueous solvent, and this invention is the following general formula (I) in this nonaqueous electrolyte.

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[0006] The nonaqueous electrolyte of this invention is used as a composition member of a lithium secondary battery. Especially about composition members other than the nonaqueous electrolyte which constitutes a rechargeable battery, it is not limited but the various composition members currently used conventionally can be used.

[0007]

[Embodiments of the Invention] In the sulfone derivative expressed with the aforementioned general formula (I) contained in the nonaqueous electrolyte by which the electrolyte is dissolved in the non-aqueous solvent, R1 and R2 become independent, respectively, and a phenyl group, a benzyl, and its an aromatic substituent like a tolyl group are desirable. Furthermore, an aliphatic substituent like the alkyl group of carbon numbers 1-12 and the cycloalkyl machine of carbon numbers 3-6 is sufficient.

[0008] As an example of a sulfone derivative expressed with the aforementioned general formula (I), diphenylsulfone, a dibenzyl sulfone, a G p-tolyl sulfone, a di-n-butyl sulfone, a G iso-butyl sulfone, a G tert-butyl sulfone, a dicyclohexyl sulfone, etc. are mentioned, for example.

[0009] Since sufficient cell performance which the cell performance might fall and was expected to be too few will not be obtained if many [ too ], the content of a sulfone derivative expressed with the aforementioned general formula (I) contained in nonaqueous electrolyte has 0.01 - 0.6% of the weight of an especially desirable range 0.001 to 2% of the weight to the weight of nonaqueous electrolyte.

[0010] As a non-aqueous solvent used by this invention, what consists of a high dielectric constant solvent and a hypoviscosity solvent is desirable. As a high dielectric constant solvent, annular carbonate, such as ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC), is mentioned suitably, for example. These high dielectric constant solvents may be used by one kind, and you may use them, combining them two or more kinds.

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capacity factor (high dielectric constant solvent : hypoviscosity solvent) — usually — 1:9-4:1 — 1:4-7:3 come out comparatively preferably, and it is used

[0012] As an electrolyte used by this invention,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ ,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ , etc. are mentioned, for example. These electrolytes may be used by one kind, and you may use them, combining them two or more kinds. 0.1–3 M of these electrolytes is usually preferably used by the concentration of 0.5–1.5M, dissolving in the aforementioned non-aqueous solvent.

[0013] The nonaqueous electrolyte of this invention is obtained by mixing an aforementioned high dielectric constant solvent and an aforementioned hypoviscosity solvent, dissolving the aforementioned electrolyte in this, and dissolving the sulfone derivative expressed with the aforementioned general formula (I).

[0014] For example, the compound metallic oxide of the at least one kind of metal and the lithium which are chosen from the group which consists of cobalt, manganese, nickel, chromium, iron, and vanadium as a positive active material is used. As such a compound metallic oxide,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , etc. are mentioned, for example.

[0015] the positive active material of the above [ a positive electrode ] — binders, such as electric conduction agents, such as acetylene black and carbon black, a polytetrafluoroethylene (PTFE), and a polyvinylidene fluoride (PVDF), and a solvent — kneading — a positive electrode — after considering as a mixture, this positive-electrode material is applied to the lath board of the aluminum foil as a charge collector, or the product made from stainless steel, and it is produced after dryness and pressurization molding by heat-treating under a vacuum at the temperature of 50 degrees C – about 250 degrees C for about 2 hours

[0016] Matter, such as a carbon material [the pyrolytic carbons, the corks, the graphite, the organic high-molecular-compounds (artificial-graphite, natural graphite, etc.) combustion object, and the carbon fiber], a compound stannic-acid ghost, etc. which have the graphite-mold crystal structure which can emit occlusion and ] a lithium metal, a lithium alloy, and a lithium as a negative-electrode active material, is used. It is desirable to use the carbon material which has especially the graphite-mold crystal structure whose spacing ( $d_{002}$ ) of a lattice plane (002) is 0.335–0.340nm (nano meter). in addition, powder material like a carbon material — binders, such as an ethylene-propylene-diene terpolymer (EPDM), a polytetrafluoroethylene (PTFE), and a polyvinylidene fluoride (PVDF), — kneading — a negative electrode — it is used as a mixture

[0017] Especially the structure of a lithium secondary battery is not limited and the coin type cell which has the separator of a positive electrode, a negative electrode and a monolayer, or a double layer, a cylindrical cell, a square shape cell which has the separator of the shape of a positive electrode, a negative electrode, and a roll further, etc. are mentioned as an example. In addition, the fine porous membrane of a polyolefine well-known as separator, textile fabrics, a nonwoven fabric, etc. are used.

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[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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EXAMPLE

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[Example] Next, an example and the example of comparison are given and this invention is explained concretely.

After having prepared the non-aqueous solvent of example 1 [manufacture of nonaqueous electrolyte] EC:DMC(capacity factor) =1:2, having dissolved so that it might become the concentration of 1M about LiPF<sub>6</sub> at this, and preparing nonaqueous electrolyte, diphenylsulfone [an R<sub>1</sub>=R<sub>2</sub>= phenyl group] was further added as a sulfone derivative (additive) so that it might become 0.1 % of the weight to nonaqueous electrolyte.

[0019] [Production of a lithium secondary battery and measurement of a cell property] What mixed acetylene black (electric conduction agent) 10% of the weight 80% of the weight, mixed the polyvinylidene fluoride (binder) at 10% of the weight of a rate, added the 1-methyl-2-pyrrolidone solvent to this, and was mixed was applied on the aluminum foil, it dried, LiCoO<sub>2</sub> (positive active material) was pressurization-cast, it heat-treated, and the positive electrode was prepared. It dried and pressurization-cast, applied what mixed the natural graphite (negative-electrode active material) 90% of the weight, mixed the polyvinylidene fluoride (binder) at 10% of the weight of a rate, added the 1-methyl-2-pyrrolidone solvent to this, and was mixed on copper foil and heat-treated, and the negative electrode was prepared. And using the separator of a polypropylene fine porosity film, the above-mentioned nonaqueous electrolyte was made to pour in and the coin cell (3.2mm in the diameter of 20mm, thickness) was produced. Using this coin cell, under the room temperature (20 degrees C), it charged to final-voltage 4.2V for 5 hours, and, next, discharged to final-voltage 2.7V under the 0.8mA constant current, and this charge and discharge were repeated by the 0.8mA constant current and the constant voltage. Initial charge-and-discharge capacity is 1M. It was almost equivalent to the case (example 1 of comparison) where LiPF<sub>6</sub>+EC-DMC (1/2) is used as nonaqueous electrolyte (with no additive), and when the cell property after 50 cycles was measured, the service-capacity maintenance factor when making initial service capacity into 100% was 92.2%. Moreover, the low-temperature property was also good. The production conditions and cell property of a coin cell are shown in Table 1.

[0020] When used diphenylsulfone [an R<sub>1</sub>=R<sub>2</sub>= phenyl group] 0.4% of the weight to nonaqueous electrolyte as example 2 additive, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 89.7%. The production conditions and cell property of a coin cell are shown in Table 1.

[0021] When used diphenylsulfone [an R<sub>1</sub>=R<sub>2</sub>= phenyl group] 0.02% of the weight to nonaqueous electrolyte as example 3 additive, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 90.8%. The production conditions and cell property of a coin cell are shown in Table 1.

[0022] When used the G p-tolyl sulfone [an R<sub>1</sub>=R<sub>2</sub>=p-tolyl group] 0.1% of the weight to nonaqueous electrolyte as example 4 additive, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 91.9%. The production conditions and cell property of a coin cell are shown in Table 1.

[0023] When used the di-n-butyl sulfone [an R<sub>1</sub>=R<sub>2</sub>=n-butyl] 0.1% of the weight to nonaqueous electrolyte as example 5 additive, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 91.6%. The production conditions and cell property of a coin cell are shown in Table 1.

[0024] The non-aqueous solvent of example 6 EC:PC:DMC(capacity factor) =1:1:2 was prepared, and after having dissolved so that it might become the concentration of 1M about LiPF<sub>6</sub> at this, and adjusting nonaqueous electrolyte, diphenylsulfone [an R<sub>1</sub>=R<sub>2</sub>= phenyl group] was further added so that it might become 0.1 % of the weight to nonaqueous electrolyte. When the coin cell was produced like the example 1 using this nonaqueous electrolyte and the cell property was measured, initial service capacity was almost equivalent to the case (example 1 of comparison) where only EC-DMC (capacity factors 1/2) is used as nonaqueous electrolyte, and when the cell property after 50 cycles was measured, the service-capacity maintenance factor when making initial service capacity into 100% was 92.3%. Moreover, the low-temperature property was also good. The production conditions and cell property of a coin cell are shown in Table 1.

[0025] When replaced with the natural graphite, and used the artificial graphite as an example 7 negative-electrode active material, and also nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 88.2%. The production conditions and cell property of a coin cell are shown in Table 1.

[0026] When replaced with LiCoO<sub>2</sub>, and used LiMn 2O<sub>4</sub> as example 8 positive active material, and also

nonaqueous electrolyte was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 91.4%. The production conditions and cell property of a coin cell are shown in Table 1.

[0027] The non-aqueous solvent of example of comparison 1 EC:DMC(capacity factor) =1:2 was prepared, and it dissolved so that it might become the concentration of 1M about LiPF<sub>6</sub> at this. At this time, the sulfone derivative was not added at all. The coin cell was produced like the example 1 using this nonaqueous electrolyte, and the cell property was measured. The service-capacity maintenance factor after 50 cycles was 83.8% to initial service capacity. The production conditions and cell property of a coin cell are shown in Table 1.

[0028]

[Table 1]

	正極	負極	添加剤	添加量 wt%	電解液組成 (容量比)	50 サイクル 放電容量維持率 %
実施例1	LiCoO <sub>2</sub>	天然黒鉛	ジフェニルスルホン	0.1	1M LiPF <sub>6</sub> EC/DMC=1/2	92.2
実施例2	LiCoO <sub>2</sub>	天然黒鉛	ジフェニルスルホン	0.4	1M LiPF <sub>6</sub> EC/DMC=1/2	89.7
実施例3	LiCoO <sub>2</sub>	天然黒鉛	ジフェニルスルホン	0.02	1M LiPF <sub>6</sub> EC/DMC=1/2	90.8
実施例4	LiCoO <sub>2</sub>	天然黒鉛	ジ-p-トリルスルホン	0.1	1M LiPF <sub>6</sub> EC/DMC=1/2	91.9
実施例5	LiCoO <sub>2</sub>	天然黒鉛	ジ-n-ブチルスルホン	0.1	1M LiPF <sub>6</sub> EC/DMC=1/2	91.6
実施例6	LiCoO <sub>2</sub>	天然黒鉛	ジフェニルスルホン	0.1	1M LiPF <sub>6</sub> EC/PC/DMC=1/1/2	92.3
実施例7	LiCoO <sub>2</sub>	人造黒鉛	ジフェニルスルホン	0.1	1M LiPF <sub>6</sub> EC/DMC=1/2	88.2
実施例8	LiMn <sub>2</sub> O <sub>4</sub>	天然黒鉛	ジフェニルスルホン	0.1	1M LiPF <sub>6</sub> EC/DMC=1/2	91.4
比較例1	LiCoO <sub>2</sub>	天然黒鉛	なし	0	1M LiPF <sub>6</sub> EC/DMC=1/2	83.8

[0029] In addition, this invention is not limited to the example of a publication, but various combination which can be guessed is easily possible for it from the meaning of invention. Especially the combination of the solvent of the above-mentioned example is not limited. Furthermore, although the above-mentioned example is related with a coin cell, this invention is applied also to the cell of cylindrical shape and prism type.

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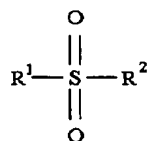
(54) 【発明の名称】 非水電解液及びそれを用いたリチウム二次電池

(57) 【要約】

【課題】 電池のサイクル特性、電気容量や充電保存特性などの電池特性に優れたリチウム二次電池を提供する。

【解決手段】 非水溶媒に電解質が溶解されている非水電解液において、該非水電解液中に下記一般式 (I)

【化1】



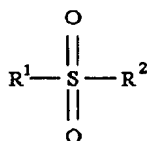
(式中、R<sup>1</sup>、R<sup>2</sup>はそれぞれ独立して、フェニル基、ベンジル基、トリル基、炭素数1から12のアルキル基、炭素数3～6のシクロアルキル基を示す。) で表されるスルホン誘導体が含有されている非水電解液、。

(2)

## 【特許請求の範囲】

【請求項1】 非水溶媒に電解質が溶解されている非水電解液において、該非水電解液中に下記一般式（I）

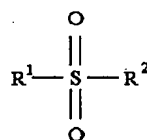
【化1】



（式中、 $\text{R}^1$ 、 $\text{R}^2$ はそれぞれ独立して、フェニル基、ベンジル基、トリル基、炭素数1～12のアルキル基、炭素数3～6のシクロアルキル基を示す。）で表されるスルホン誘導体が含有されていることを特徴とする非水電解液。

【請求項2】 正極、負極および非水溶媒に電解質が溶解されている非水電解液～なるリチウム二次電池において、該非水電解液中に下記一般式（I）

【化2】



（式中、 $\text{R}^1$ 、 $\text{R}^2$ はそれぞれ独立して、フェニル基、ベンジル基、トリル基、炭素数1～12のアルキル基、炭素数3～6のシクロアルキル基を示す。）で表されるスルホン誘導体が含有されていることを特徴とするリチウム二次電池。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、電池のサイクル特性や電気容量、保存特性などの電池特性にも優れたリチウム二次電池を提供することができる非水電解液、およびそれを用いたリチウム二次電池に関する。

【0002】

【従来の技術】 近年、リチウム二次電池は小型電子機器などの駆動用電源として広く使用されている。リチウム二次電池は、主に正極、非水電解液及び負極～構成されており、特に、 $\text{LiCoO}_2$ などのリチウム複合酸化物を正極とし、炭素材料又はリチウム金属を負極としたリチウム二次電池が好適に使用されている。そして、そのリチウム二次電池用の非水電解液としては、エチレンカーボネート（EC）、プロピレンカーボネート（PC）などのカーボネート類が好適に使用されている。

【0003】

【発明が解決しようとする課題】 しかしながら、電池のサイクル特性および電気容量などの電池特性について、さらに優れた特性を有する二次電池が求められている。正極として、例えば $\text{LiCoO}_2$ 、 $\text{LiMn}_2\text{O}_4$ 、 $\text{LiNiO}_2$ などを用いたリチウム二次電池は、非水電解液

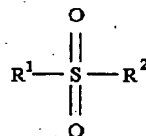
中の溶媒が充電時に局部的に一部酸化分解することにより、該分解物が電池の望ましい電気化学的反応を阻害するために電池性能の低下を生じる。これは正極材料と非水電解液との界面における溶媒の電気化学的酸化に起因するものと思われる。また、負極として例えば天然黒鉛や人造黒鉛などの高結晶化した炭素材料を用いたリチウム二次電池は、非水電解液中の溶媒が充電時に負極表面で還元分解し、非水電解液溶媒として一般に広く使用されているECにおいても充放電を繰り返す間に一部還元分解が起こり、電池性能の低下が起こる。このため、電池のサイクル特性および電気容量などの電池特性は必ずしも満足なものではないのが現状である。

【0004】 本発明は、前記のようなリチウム二次電池用非水電解液に関する課題を解決し、電池のサイクル特性に優れ、さらに電気容量や充電状態での保存特性などの電池特性にも優れたリチウム二次電池を構成することができるリチウム二次電池用の非水電解液、およびそれを用いたリチウム二次電池を提供することを目的とする。

20 【0005】

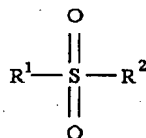
【課題を解決するための手段】 本発明は、非水溶媒に電解質が溶解されている非水電解液において、該非水電解液中に下記一般式（I）

【化3】



30 （式中、 $\text{R}^1$ 、 $\text{R}^2$ はそれぞれ独立して、フェニル基、ベンジル基、トリル基、炭素数1～12のアルキル基、炭素数3～6のシクロアルキル基を示す。）で表されるスルホン誘導体が含有されていることを特徴とする非水電解液に関する。また、本発明は、正極、負極および非水溶媒に電解質が溶解されている非水電解液からなるリチウム二次電池において、該非水電解液中に下記一般式（I）

【化4】



（式中、 $\text{R}^1$ 、 $\text{R}^2$ はそれぞれ独立して、フェニル基、ベンジル基、トリル基、炭素数1～12のアルキル基、炭素数3～6のシクロアルキル基を示す。）で表されるスルホン誘導体が含有されていることを特徴とするリチウム二次電池に関する。

【0006】 本発明の非水電解液は、リチウム二次電池の構成部材として使用される。二次電池を構成する非水



(3)

電解液以外の構成部材については特に限定されず、従来使用されている種々の構成部材を使用できる。

【0007】

【発明の実施の形態】非水溶媒に電解質が溶解されている非水電解液に含有される前記一般式(I)で表されるスルホン誘導体において、 $R^1$ 、 $R^2$ はそれぞれ独立して、フェニル基、ベンジル基、トリル基のような芳香族の置換基が好ましい。更には、炭素数1~12のアルキル基、炭素数3~6のシクロアルキル基のような脂肪族の置換基でもよい。

【0008】前記一般式(I)で表されるスルホン誘導体の具体例としては、例えば、ジフェニルスルホン、ジベンジルスルホン、ジ-p-トリルスルホン、ジ-n-ブチルスルホン、ジ-is-o-ブチルスルホン、ジ-tert-ブチルスルホン、ジシクロヘキシルスルホンなどが挙げられる。

【0009】非水電解液中に含有される前記一般式(I)で表されるスルホン誘導体の含有量は、過度に多いと電池性能が低下することがあり、また、過度に少ないと期待した十分な電池性能が得られないので、非水電解液の重量に対して0.001~2重量%、特に0.01~0.6重量%の範囲が好ましい。

【0010】本発明で使用される非水溶媒としては、高誘電率溶媒と低粘度溶媒とからなるものが好ましい。高誘電率溶媒としては、例えば、エチレンカーボネート(EC)、プロピレンカーボネート(PC)、ブチレンカーボネート(BC)などの環状カーボネート類が好適に挙げられる。これらの高誘電率溶媒は、一種類で使用してもよく、また二種類以上組み合わせて使用してもよい。

【0011】低粘度溶媒としては、例えば、ジメチルカーボネート(DMC)、メチルエチルカーボネート(MEC)、ジエチルカーボネート(DEC)などの鎖状カーボネート類、テトラヒドロフラン、2-メチルテトラヒドロフラン、1,4-ジオキサン、1,2-ジメトキシエタン、1,2-ジエトキシエタン、1,2-ジブトキシエタンなどのエーテル類、 $\gamma$ -ブチロラクトンなどのラクトン類、アセトニトリルなどのニトリル類、プロピオン酸メチルなどのエステル類、ジメチルホルムアミドなどのアミド類が挙げられる。これらの低粘度溶媒は一種類で使用してもよく、また二種類以上組み合わせて使用してもよい。高誘電率溶媒と低粘度溶媒とはそれぞれ任意に選択され組み合わせて使用される。なお、前記の高誘電率溶媒および低粘度溶媒は、容量比(高誘電率溶媒:低粘度溶媒)で通常1:9~4:1、好ましくは1:4~7:3の割合で使用される。

【0012】本発明で使用される電解質としては、例えば、 $LiPF_6$ 、 $LiBF_4$ 、 $LiClO_4$ 、 $LiN(SO_2CF_3)_2$ 、 $LiN(SO_2C_2F_5)_2$ 、 $LiC(SO_2CF_3)_3$ などが挙げられる。これらの電解質

4

は、一種類で使用してもよく、二種類以上組み合わせて使用してもよい。これら電解質は、前記の非水溶媒に通常0.1~3M、好ましくは0.5~1.5Mの濃度で溶解されて使用される。

【0013】本発明の非水電解液は、例えば、前記の高誘電率溶媒や低粘度溶媒を混合し、これに前記の電解質を溶解し、前記一般式(I)で表されるスルホン誘導体を溶解することにより得られる。

【0014】例えば、正極活物質としてはコバルト、マンガン、ニッケル、クロム、鉄およびバナジウムからなる群より選ばれる少なくとも一種類の金属とリチウムとの複合金属酸化物が使用される。このような複合金属酸化物としては、例えば、 $LiCoO_2$ 、 $LiMn_2O_4$ 、 $LiNiO_2$ などが挙げられる。

【0015】正極は、前記の正極活物質をアセチレンブラック、カーボンブラックなどの導電剤、ポリテトラフルオロエチレン(PTFE)、ポリフッ化ビニリデン(PVDF)などの結着剤および溶剤と混練して正極合剤とした後、この正極材料を集電体としてのアルミニウム箔やステンレス製のラス板に塗布して、乾燥、加圧成型後、50℃~250℃程度の温度で2時間程度真空中で加熱処理することにより作製される。

【0016】負極活物質としては、リチウム金属やリチウム合金、およびリチウムを吸蔵・放出可能な黒鉛型結晶構造を有する炭素材料(熱分解炭素類、コークス類、グラファイト類(人造黒鉛、天然黒鉛など)、有機高分子化合物燃焼体、炭素繊維)や複合スズ酸化物などの物質が使用される。特に、格子面(002)の面間隔(d002)が0.335~0.340nm(ナノメートル)である黒鉛型結晶構造を有する炭素材料を使用することが好ましい。なお、炭素材料のような粉末材料はエチレンプロピレンジエンターポリマー(EPDM)、ポリテトラフルオロエチレン(PTFE)、ポリフッ化ビニリデン(PVDF)などの結着剤と混練して負極合剤として使用される。

【0017】リチウム二次電池の構造は特に限定されるものではなく、正極、負極および単層又は複層のセパレータを有するコイン型電池、さらに、正極、負極およびロール状のセパレータを有する円筒型電池や角型電池などが一例として挙げられる。なお、セパレータとしては公知のポリオレフィンの微多孔膜、織布、不織布などが使用される。

【0018】

【実施例】次に、実施例および比較例を挙げて、本発明を具体的に説明する。

実施例1

【非水電解液の調製】EC:DMC(容量比)=1:2の非水溶媒を調製し、これに $LiPF_6$ を1Mの濃度になるように溶解して非水電解液を調製した後、さらにスルホン誘導体(添加剤)としてジフェニルスルホン[R

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 $R^1=R^2$ =フェニル基]を非水電解液に対して0.1重量%となるように加えた。

【0019】〔リチウム二次電池の作製および電池特性の測定〕 $LiCoO_2$  (正極活物質)を80重量%、アセチレンブラック (導電剤)を10重量%、ポリフッ化ビニリデン (結着剤)を10重量%の割合で混合し、これに1-メチル-2-ピロリドン溶剤を加えて混合したものをアルミニウム箔上に塗布し、乾燥、加圧成型、加熱処理して正極を調製した。天然黒鉛 (負極活物質)を90重量%、ポリフッ化ビニリデン (結着剤)を10重量%の割合で混合し、これに1-メチル-2-ピロリドン溶剤を加え、混合したものを銅箔上に塗布し、乾燥、加圧成型、加熱処理して負極を調製した。そして、ポリプロピレン微多孔性フィルムのセパレータを用い、上記の非水電解液を注入させてコイン電池 (直径20mm、厚さ3.2mm)を作製した。このコイン電池を用いて、室温(20℃)下、0.8mAの定電流及び定電圧で、終止電圧4.2Vまで5時間充電し、次に0.8mAの定電流下、終止電圧2.7Vまで放電し、この充電電を繰り返した。初期放電容量は、1M  $LiPF_6$  + EC-DMC (1/2)を非水電解液 (添加剤無し)として用いた場合 (比較例1)とほぼ同等であり、50サイクル後の電池特性を測定したところ、初期放電容量を100%としたときの放電容量維持率は92.2%であった。また、低温特性も良好であった。コイン電池の作製条件および電池特性を表1に示す。

#### 【0020】実施例2

添加剤として、ジフェニルスルホン [ $R^1=R^2$ =フェニル基]を非水電解液に対して0.4重量%使用したほかは実施例1と同様に非水電解液を調製してコイン電池を作製し、50サイクル後の電池特性を測定したところ、放電容量維持率は89.7%であった。コイン電池の作製条件および電池特性を表1に示す。

#### 【0021】実施例3

添加剤として、ジフェニルスルホン [ $R^1=R^2$ =フェニル基]を非水電解液に対して0.02重量%使用したほかは実施例1と同様に非水電解液を調製してコイン電池を作製し、50サイクル後の電池特性を測定したところ、放電容量維持率は90.8%であった。コイン電池の作製条件および電池特性を表1に示す。

#### 【0022】実施例4

添加剤として、ジ-p-トリルスルホン [ $R^1=R^2$ =p-トリル基]を非水電解液に対して0.1重量%使用したほかは実施例1と同様に非水電解液を調製してコイン電池を作製し、50サイクル後の電池特性を測定したと

ころ、放電容量維持率は91.9%であった。コイン電池の作製条件および電池特性を表1に示す。

#### 【0023】実施例5

添加剤として、ジ-n-ブチルスルホン [ $R^1=R^2$ =n-ブチル基]を非水電解液に対して0.1重量%使用したほかは実施例1と同様に非水電解液を調製してコイン電池を作製し、50サイクル後の電池特性を測定したところ、放電容量維持率は91.6%であった。コイン電池の作製条件および電池特性を表1に示す。

#### 【0024】実施例6

EC:PC:DMC (容量比)=1:1:2の非水溶媒を調製し、これに $LiPF_6$ を1Mの濃度になるように溶解して非水電解液を調整した後、さらにジフェニルスルホン [ $R^1=R^2$ =フェニル基]を非水電解液に対して0.1重量%となるように加えた。この非水電解液を使用して実施例1と同様にコイン電池を作製し、電池特性を測定したところ、初期放電容量はEC-DMC (容量比1/2)のみを非水電解液として用いた場合 (比較例1)とほぼ同等であり、50サイクル後の電池特性を測定したところ、初期放電容量を100%としたときの放電容量維持率は92.3%であった。また、低温特性も良好であった。コイン電池の作製条件および電池特性を表1に示す。

#### 【0025】実施例7

負極活物質として、天然黒鉛に代えて人造黒鉛を使用したほかは実施例1と同様に非水電解液を調製してコイン電池を作製し、50サイクル後の電池特性を測定したところ、放電容量維持率は88.2%であった。コイン電池の作製条件および電池特性を表1に示す。

#### 【0026】実施例8

正極活物質として、 $LiCoO_2$ に代えて $LiMn_2O_4$ を使用したほかは実施例1と同様に非水電解液を調製してコイン電池を作製し、50サイクル後の電池特性を測定したところ、放電容量維持率は91.4%であった。コイン電池の作製条件および電池特性を表1に示す。

#### 【0027】比較例1

EC:DMC (容量比)=1:2の非水溶媒を調製し、これに $LiPF_6$ を1Mの濃度になるように溶解した。このときスルホン誘導体は全く添加しなかった。この非水電解液を使用して実施例1と同様にコイン電池を作製し、電池特性を測定した。初期放電容量に対し、50サイクル後の放電容量維持率は83.8%であった。コイン電池の作製条件および電池特性を表1に示す。

#### 【0028】

【表1】

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	正極	負極	添加剤	添加量 wt%	電解液組成 (容量比)	50 サイクル 放電容量維持率 %
実施例1	$\text{LiCoO}_2$	天然 黒鉛	ジフェニル スルホン	0.1	1M $\text{LiPF}_6$ EC/DMC=1/2	92.2
実施例2	$\text{LiCoO}_2$	天然 黒鉛	ジフェニル スルホン	0.4	1M $\text{LiPF}_6$ EC/DMC=1/2	89.7
実施例3	$\text{LiCoO}_2$	天然 黒鉛	ジフェニル スルホン	0.02	1M $\text{LiPF}_6$ EC/DMC=1/2	90.8
実施例4	$\text{LiCoO}_2$	天然 黒鉛	ジ-p-トリル スルホン	0.1	1M $\text{LiPF}_6$ EC/DMC=1/2	91.9
実施例5	$\text{LiCoO}_2$	天然 黒鉛	ジ-n-ブチル スルホン	0.1	1M $\text{LiPF}_6$ EC/DMC=1/2	91.6
実施例6	$\text{LiCoO}_2$	天然 黒鉛	ジフェニル スルホン	0.1	1M $\text{LiPF}_6$ EC/PC/DMC=1/1/2	92.3
実施例7	$\text{LiCoO}_2$	人 造 黒鉛	ジフェニル スルホン	0.1	1M $\text{LiPF}_6$ EC/DMC=1/2	88.2
実施例8	$\text{LiMn}_2\text{O}_4$	天然 黒鉛	ジフェニル スルホン	0.1	1M $\text{LiPF}_6$ EC/DMC=1/2	91.4
比較例1	$\text{LiCoO}_2$	天然 黒鉛	なし	0	1M $\text{LiPF}_6$ EC/DMC=1/2	83.8

【0029】なお、本発明は記載の実施例に限定されず、発明の趣旨から容易に類推可能な様々な組み合わせが可能である。特に、上記実施例の溶媒の組み合わせは限定されるものではない。更には、上記実施例はコイン電池に関するものであるが、本発明は円筒形、角柱形の

電池にも適用される。

【0030】

【発明の効果】本発明によれば、電池のサイクル特性、電気容量、保存特性などの電池特性に優れたリチウム二次電池を提供することができる。

フロントページの続き

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